

THIN LAYER OF HAFNIUM OXIDE AND DEPOSIT PROCESSDESCRIPTIONField of the invention

The invention relates to the field of thin layers of hafnium oxide or stacks of thin layers comprising at least one layer of hafnium oxide. It also concerns a process for producing thin layers of hafnium oxide.

5 These thin layers are layers appearing in multilayer structures incorporating, apart from hafnium oxide layers, layers of other compositions.

Prior art

10 The deposit of thin layers of hafnium oxide, just like many other deposits, is carried out in known fashion by evaporation under vacuum. The basic principle is as follows:

In a vacuum chamber, an electron gun heats a target constituted of the material to be deposited. The material is then vaporised and deposited on a substrate, which has been placed close by. In the case of an oxide deposit, one can also carry out the same operation starting from the product to be oxidised, for

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20 example a metal, the vacuum chamber containing oxygen under very low pressure. The latter procedure is known under the name "reactive evaporation under oxygen".

In the case of hafnium oxide, the two techniques are used but for reasons which will be set out below,

25 they are always associated with energy means such as direct heating of the substrate, ion bombardment of the

layer during growth, or furthermore acceleration of the ions of the material to be deposited by means of an electric field, in such a way that they provide energy to the substrate.

5       The deposit processes are described in a more detailed way, for example in the manual by J.D. RANCOURT "Optical thin film user handbook, SPIE Press, 1996" (C1).

10       The production of layers of hafnium oxide or hafnia ( $\text{HfO}_2$ ) is used mainly in multilayer coatings of optical components submitted to high laser fluxes. The function of the hafnia layers can be to ensure protection of the components to which they are added.

15       The component incorporating such layers of hafnia can in itself ensure protection against the laser flux and the optical function of the component. The multilayer composition can also be deposited as a protective coating on a pre-existing optical component to attenuate the laser flux undergone by this optical  
20       component. The hafnia layers ensure protection in the wavelength ranges extending from the ultraviolet to the infrared for any type of laser, impulse or continuous.

25       The multilayer components incorporating the hafnia layers ensure the optical functions for example of mirror, spectral filter or anti-reflection.

30       The production of these special optical functions requires the production of surface treatments. It concerns, by suitable stacking of materials with different refraction indices, creation of an interferential system, which creates the desired optical function.

In order to do this, two or more materials are used, deposited alternately. In general, two materials, one with a high index and the other with a low index, suffice for the majority of applications.

5 Many materials can be used to play this role. For example, the following can be cited:

- silicon dioxide or silica ( $\text{SiO}_2$ )
- alumina ( $\text{Al}_2\text{O}_3$ )
- titanium dioxide ( $\text{TiO}_2$ )
- 10 - Yttrium fluoride  $\text{YF}_3$

In the special case of optics submitted to high laser fluxes, the laser damage threshold (LDT) of stacks is defined as the value of the fluence (or energy received per surface unit) above which appears a  
15 permanent modification of surface treatment. Indications about the modes for producing layers with high damage thresholds can be found in a book by M.R. Kozlowski "Thin film for Optical Systems" published by F.R. Flory in 1995, (C2). Chapter 17 of this book  
20 page 521 and following, provide the present trends in the choice of the material constituting the layers, the methods for measuring damage and deposit methods. In this chapter, especially in paragraph 3-5 pages 536-537, it is especially indicated that the deposit  
25 techniques with energy means, as for example, with ion bombardment, have become very widely used because of the improved possibilities of controlling the thickness and the mechanical stability of the layer. These processes lead to layers with limited defects.

30 The damage to optical components is the factor limiting the maximum working laser fluences. This

motivates research into improving laser damage thresholds for surface treatments.

Within this framework, numerous families of materials were studied, for example, fluoride, 5 chalcogenide and oxide materials. The latter have been studied the most within the framework of surface treatments presenting high laser damage thresholds.

For applications with high laser flux in the near infrared, the  $\text{HfO}_2/\text{SiO}_2$  couple is usually used, given 10 the high laser damage thresholds of the components obtained. Examples of results obtained with this couple are described in diverse applications. These publications in general indicate in which manner the layers were deposited. Examples of such publications 15 are given below, for information and for better understanding of what is to follow. An article by Allan J. WARLDORF et Al. published the 1.10.93 in the revue "Applied Optics" Vol. 32 No. 28, pages 5583-5593 (C3) describes the methods and results obtained concerning 20 the laser damage threshold with this couple. This article explains (in particular page 5583, second column) that the evaporation processes by heating the product to be evaporated by heating resistance or by electron beam give rapid but unsatisfactory results, in 25 particular from the point of view of damage thresholds. It indicates that the porosity of the films can be reduced by raising the temperature of the substrate, or by acceleration of the ions to be deposited.

It is also indicated that the results obtained 30 with the methods of ion acceleration (ion plating) have encouraged filter manufacturers to use this method

which therefore has tended to be generalised (p. 5584 top of column 2).

Other articles, for example BRAUN et al. entitled "Optical coating for high-power neodymium lasers" published in the review SOV. J. Quantum Electron 18 (10) - 1988 - page 1286-1290 (C4) or again that of L.L. Chase et al., "Investigation of optical damage in hafnia and silica thin films using pairs of sub-nanosecond laser pulses with variable time delay, J. Applied Physics, 71(3)(1992), pages 1204-1208" (C5) give damage results obtained with refractory oxide layers and in particular with hafnium oxides.

In the two articles quoted above, (C4-C5), the coatings were obtained by electron beam evaporation. In the second article (C5) it is indicated (page 1204, bottom of column 2) that the substrates were maintained at a temperature of 200°C during deposit.

In the great majority of published works, the coatings are produced by evaporation under vacuum from a hafnium oxide precursor.

Among the references already given above, on this subject, one can mention documents C2, C4, C5 and also the article by R.J. Tench et al., "Characterization of defects geometries in multilayer optical coatings, J. Vac. Sci. Technol. A 12(5) (1994) pp 2808" (C6)

This elaboration technique, directly from the oxide, has the inconvenience of generating many defects in the coatings due to projections issuing from the oxide load during evaporation.

These defects buried in the stack are identified as precursors of optical damage under laser flux.

Relative to this subject, one can consult the article of R. Chow et al., "Reactive evaporation of low-defect density hafnia, Applied Optics. Vol. 32 No. 28 (1993) pp 5567" (C7).

5        There are few publications openly available relative to the production of components from reactive evaporation of metallic hafnium under oxygen.

      Apart from document C7, already mentioned above, it is however possible to cite the article by J.F. Anzellotti et al., "Stress and environmental shift characteristics of  $\text{HfO}_2/\text{SiO}_2$  multilayer coating. Proceedings of the 28th annual Boulder Damage Symposium, SPIE Vol. 2966 (1996)" (C8).

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      In document C7, the results obtained by the evaporation techniques of hafnium metal and hafnia are compared.

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      Although they present attractive results concerning the reduction of the density and defects of nodular type, the authors do not demonstrate an improvement of laser damage thresholds for coatings produced by reactive evaporation of metal under oxygen. It can be thought that the presence of nodules in the coatings does not constitute a laser damage factor until the ultimate performance of the materials has been reached.

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      Taking into account the state of the art, the inventors considered that it was possible to obtain good results concerning laser damage resistance, for the production of layers ensuring optical functions for example of the mirror, spectral filter or antireflection type, from the reactive evaporation of

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metallic hafnium under oxygen, but on condition of mastering the growth conditions of the layers in particular the formation of aggregates and crystallinity.

5        It is known, for example from the article by B.A. Movchan et al. Fiz. Met. Mettaloved, 28 (1969) pp 653 (C9) that the structure and properties of condensates of metals or oxides depend closely on the temperature of the substrate on which the condensation takes place.

10       Therefore, the inventors tried to understand better the crystalline growth and the formation of metal aggregates and thus the ways to avoid them.

Non-energy processes with evaporation base produce coatings with high porosity.

15       In fact, the energy of evaporated species is relatively low: it is a function of the evaporation temperature of the material but typically of the order of several tenths of electron volts (eV). This leads to a very low mobility of species which condense on the  
20       surface of the substrate. In the time interval corresponding to the deposit of two successive atom mono-layers, the atom displacements are not sufficient for inducing the compaction of layers and these vacancies are "buried". In this way, a microstructure  
25       of porous layers is induced, characteristic of deposits obtained by evaporation. The consequence of this is the production of layers more difficult to control, for the following reasons:

30       - appearance of mechanical tension stresses in the layers which do not favour the stability of the stacks

unless specific compensation mechanisms are put into operation;

- evolution with time of the optical response of the component (progressive filling of porosities by water, inducing slipping of the average refraction index);

- process drift, the share of the thermal radiation of the evaporation loads being no longer negligible on a non-heated substrate. This means that the temperature of the substrate on which the deposit is made increases, and consequently the mobility of the species which condense on the substrate.

To minimise or annul the phenomena mentioned above, the great majority of processes implement means making it possible to densify the coatings. In order to do this, those skilled in the art possess techniques allowing an energy input on coatings during growth: the heating of substrates and ion bombardment of layers during growth.

As seen above, these techniques, providing the substrate with an input of energy, are very widely used in evaporation processes for thin layers.

The inventors have shown that these techniques degraded the performances of thin layers in terms of laser damage threshold at 1.06  $\mu\text{m}$ .

This idea is based on studies on the damage of thin layers by lasers. Results of these studies have been published by J. Dijon et al., Nano absorbing center: a key point in laser damage of thin films. Proc. of 28th annual Boulder Damage Symposium, SPIE Vol. 2996 (1996) (C10). It is to be noted that one of



the authors of this publication is also one of the inventors. The results of these studies are that the presence of metallic impurities under aggregate form in the coatings provokes, via the creation of a relay  
5 mechanism of heating of aggregates and radiation in the far ultraviolet, a local transformation of the layers rendering them absorbent to laser radiation at 1.06  $\mu\text{m}$ , then the coupling of the laser on the material and destruction of the coating.

10 It is difficult to avoid the presence of metallic impurities within surface treatments whether they are impurities of external origin (material from the evaporation crucible, impurities from the evaporation load, constitutive elements of the evaporation chamber  
15 in the case of utilisation of an ion source) or incompletely oxidised hafnium atoms.

When heating, or which comes to the same from the point of view of energy input to the substrate, when bombarding the layer with ions during growth,  
20 crystallisation of the deposit is encouraged.

It is known that grain boundaries present in a crystallised material constitute privileged pathways for diffusion of impurities. An amorphous structure can "freeze" the diffusion of these impurities.

25 According to observations made by the inventors, the phenomenon of crystallisation of hafnia is necessarily induced by the energy supplied to the substrate by heating or by ion bombardment. This crystallisation is revealed by peaks of X-ray  
30 diffraction. The crystallisation characteristic of the energy input is also revealed by transmission electron

microscopy. With this method the crystalline planes diffract the electrons in precise directions giving well defined rings from which it is possible to determine the crystalline structure of the material, for example a monoclinic structure for a deposit carried out on a substrate heated to 200°C.

#### Brief description of the invention

Taking into account the state of the art which has just been described, the inventors thought that any energy input is unfavourable for withstanding laser flux since it will encourage the stabilisation of these impurities by the formation of aggregates.

The basic idea of the invention, which goes contrary to the usual concepts of those skilled in the art, consists of working on a non-energy process, that is to say without either ionic assistance or heating of the substrates.

The materials deposited are thus amorphous, that is to say non-crystalline. In addition, when working with an energy input, one creates a compaction of the layer deposited. On the contrary, the material deposited without energy input has a lower density. In the inventors' documentation no data was found relating to the density of the hafnia layers deposited by known processes. The lowest densities known to the inventors are 8.5 gm/cm<sup>3</sup>. The densities measured on the hafnia layers according to the invention range between 6.4 and 8.1 gm/cm<sup>3</sup>. These densities can be measured by X-ray reflectometry. As pointed out above, crystallisation only intervenes if the substrates are

heated or, which comes to the same thing from the point of view of energy input, if the layer is bombarded with ions during growth. The absence of crystallisation, according to the inventors, can also explain the  
5 reduction of the formation of aggregates because, as already mentioned above, grain boundaries present in a crystallised material constitute privileged pathways for diffusion of impurities. An amorphous structure can "freeze" the diffusion of these impurities.

10 To summarise, the invention relates to a thin layer of hafnium oxide characterised in that the hafnium oxide is in amorphous form with a density lower than  $8 \text{ gm/cm}^3$ .

Contrary to the layers of hafnium oxides of prior  
15 art, an amorphous layer of hafnium oxide does not show any X-ray diffraction peak. Observation by transmission electron microscopy shows diffuse rings characteristic of an amorphous structure. The invention also relates to a stack of thin layers characterised in that it  
20 comprises at least one layer of amorphous hafnium oxide of density lower than  $8 \text{ gm/cm}^3$  or, furthermore, to an optical component with a surface treatment characterised in that said surface treatment comprises at least one layer of amorphous hafnium oxide of  
25 density lower than  $8 \text{ gm/cm}^3$ .

In general, said layer of amorphous hafnium oxide of density lower than  $8 \text{ gm/cm}^3$  is part of a stack of layers comprising at least one layer with a refraction index different from that of hafnium oxide.

30 Finally, the invention relates to a process for depositing under vacuum on a substrate at least one

layer of hafnium oxide by reactive evaporation under oxygen of metallic hafnium, said process characterised in that the deposit is carried out without any energy input to the substrate, whether or not this input is  
5 before the deposit or during the deposit.

When one says that there is no energy input, this means that on the one hand the substrate is not heated or pre-heated, and on the other hand that no energy process is used such as ion bombardment of the layer  
10 during growth, or ion acceleration before deposit (ion plating). The deposit is a "natural" deposit through the simple effect of condensation of the material to be deposited on the substrate. This deposit is then amorphous, that is to say there is an absence of  
15 crystallinity.

As indicated above, the main advantage provided by layers of amorphous hafnia according to the invention is the very high resistance to laser flux.

The hafnia mono-layer according to the invention,  
20 deposited on silica, was able to withstand a laser flux higher than 15 Joules/cm<sup>2</sup> at a wavelength of 1.06  $\mu$ m with impulses of 3 nsec with a recurrence frequency of 10 Hz until obtaining 15 Joules/cm<sup>2</sup>. The best prior art known to the inventors is situated, under the same  
25 conditions, in a range from 3 to 5 Joules/cm<sup>2</sup>.

Furthermore, the cold process according to the invention allows a very substantial gain in time for the deposit chamber cycle.

In fact, heating the substrates can immobilise the  
30 deposit equipment for a whole day when treating the most voluminous pieces, for example mirrors for the

Megajoule laser beam carrier. This mirror will be described below.

With the cold process according to the invention, the production of this type of mirror requires a time cycle of 5 hours (not including putting the chamber under vacuum). It is therefore possible to carry out one deposit cycle per day, even if it were shown that a cooling of components between each hafnia deposit significantly improves the performance of the components.

Finally, with the process according to the invention, it is not necessary to make deposits on substrates with high thermal stability.

In the production carried out so far, it has not been necessary to cool the substrate actively, nor to control its temperature in a precise fashion.

For deposits of several mono-layers, the time required is short enough not to provoke significant temperature rise; for thicker deposits, two stages were applied (or more if necessary) interrupted by free cooling time (for example, overnight). It is also possible to envisage cooling time after the deposit of each layer of  $\text{HfO}_2$ . These cooling periods typically last for a time equivalent to one or several deposit times of the preceding layer.

It is also possible, in order to reduce the time of utilisation of the chamber for a special mono-layer or multilayer production, to cool the substrate actively during growth of the deposit or during an interruption period of the deposit.

Brief description of the drawings

Examples of production of stacks of thin layers among which amorphous hafnia layers according to the invention will now be described with reference to the  
5 attached drawings in which:

- Figure 1 shows a cross-section of a substrate carrying a layer of amorphous hafnium oxide according to the invention.

- Figures 2 and 3 show comparisons between plots  
10 of X-ray diffraction:

- Figure 2 between layers of hafnium oxide comprising oxide crystals resulting from heating of the substrate and an amorphous layer according to the invention,

15 - figure 3 between a layer of hafnium oxide comprising crystals of hafnium oxide resulting from ion bombardment of the substrate and an amorphous layer according to the invention.

- Figure 4 shows a cross-section of a substrate  
20 carrying a stack composed of layers of amorphous hafnium oxide according to the invention and layers of silicon oxide, the stack ensuring a mirror function.

- Figure 5 is a curve representing the reflection of a mirror component of figure 4 in function of  
25 wavelength.

- Figure 6 is a partial cross-section of an optical component comprising a stack of alternate layers of amorphous hafnia and silicon oxide.

- Figure 7 is a curve representing the optical  
30 performances of an anti-reflection component in terms

of percentage of transmission of light in the working spectrum range.

- Figure 8 is a curve representing the values of transmission of a silica substrate in the 800-2600 nm range treated with a stack of 10 layers of  $\text{HfO}_2$  and  $\text{SiO}_2$  of total thickness 2300 nm.

Description of examples of production of stacks of layers comprising layers according to the invention

Figure 1 shows a layer of amorphous hafnium oxide 2, according to the invention, deposited on a substrate 1. It can be checked that the hafnium oxide is amorphous, for example, by observation of the X-ray diffraction plot.

Such plots are shown in figures 2 and 3.

Figure 2 shows curves 7, 8, 9, 10. The curves represent in arbitrary units, the intensity of X-rays diffracted depending upon the value of the angle of diffraction.

Curve 7 shows the diffraction spectrum of a layer of hafnia produced cold (without heating of the deposit substrate).

Curves 8, 9 and 10 show diffraction spectra of a hafnia layer produced with a deposit substrate of 100°, 150° and 200°C respectively.

Figure 3 shows two curves 11 and 12. These curves show the diffraction spectra of hafnia layers produced either without ion bombardment of the layer during growth (curve 11), or with ion bombardment (curve 12).

Curves 7 and 11 do not reveal any diffraction peaks 13: the layers of hafnia are thus amorphous.

On the other hand, layers 8, 9, 10 and 12 reveal diffraction peaks 13 characteristic of crystalline materials.

The following examples of embodiments are produced  
5 by stacks of layers of  $\text{HfO}_2/\text{SiO}_2$  for the reasons given above.

The layers of amorphous hafnium oxide are deposited cold according to the process of the invention, as are the layers of silicon oxide,  
10 deposited without deliberate heating nor ion bombardment of the substrates.

A first embodiment example relates to the production of a mirror 4 at 1064 nm. The component 4 must ensure a reflecting function at 1064 nm under an  
15 angle of incidence of  $45^\circ$ . This mirror 4 is produced by a stack of formula 12 (HB)  $\text{H}_2\text{B}$  where H represents a mono-layer of thickness 156 nm of  $\text{HfO}_2$  and B a mono-layer of 213 nm of  $\text{SiO}_2$ .

A cross-section of this optical component 4  
20 intended to represent the stacking of the layers is shown in figure 4. On a substrate 1, the mirror according to the invention comprises first of all a stack of twelve layers H of amorphous hafnium oxide 2, each alternating with a layer B of silicon oxide 3. It  
25 then comprises two layers H of amorphous hafnium oxide 2 and finally a layer B of silicon oxide 3.

In order to produce such thick stacks, the radiation of hafnium raised to more than  $2000^\circ\text{C}$  creates a progressive rise in the temperature by direct  
30 radiation on the substrates. If no special precautions are taken, it is estimated from thermocouple



measurements that the temperature approaches 100°C at the end of evaporation. It is possible to reduce this rise in temperature by interrupting the process by periods of cooling. In this embodiment the reflecting layer was obtained in two stages with a phase of natural cooling half-way through the stacking. Figure 5 shows the reflection of the component in function of wavelength. Reflection reaches 99.5% at 1200 nm. Measurement at an angle of incidence of 45° gives a reflectivity higher than 99% at 1064 nm. A damage test was carried out with increasing fluence according to the "R On 1" method described on page 523 of document C2. According to this method, each test zone is illuminated with increasing series of several hundreds of impulses, here of 3 nanoseconds each, with a recurrence frequency of 10 Hertz, of increasing fluence. The average damage thresholds measured are of the order of 50 Joules/cm<sup>2</sup>, that is to say a value much higher than any mentioned in present publications. Thus Waldorf et al. report in document C3 that they obtained values of threshold laser damage at 1.06 µm lower than 2 Joules/cm<sup>2</sup> from hafnium evaporation, but with ion bombardment, (species energy Ar<sup>+</sup> and O<sub>2</sub><sup>+</sup> which bombard the substrate during growth of the order of 40 eV in this study) thus energy input to the substrate which results in crystallisation of the hafnium oxide contrary to the process of the invention which itself is without energy input and results in layers of amorphous hafnium oxide.

The inventors consider that these good results are due to the absence of metallic aggregates and/or the

amorphous form of the hafnia layers according to the invention whereas on the contrary, according to prior art, the energy input resulted in crystallisation of the material.

5       The second example is relative to a surface anti-reflection treatment in the wavelength range of 550 to 670 nm. This treatment can, for example, be used as treatment for an optical component in a SILVA laser chain used for the isotopic separation by laser of  
10       uranium in vapour phase. A stack of six layers of  $\text{HfO}_2/\text{SiO}_2$  of total thickness 630 nm was deposited on each of the faces of a substrate, the layers of amorphous hafnia being deposited by the process according to the invention.

15       In figure 6, the optical component 6 is shown, with the aim of simplification, with a single example of the two-layer composition comprising a layer of amorphous hafnia 2 alternating with a layer of silicon oxide 3.

20       The curve in figure 7 shows the optical performances of component 6 in terms of percentage of light transmission in the working spectral range expressed in nm. It can be seen that the percentage is very close to 100% within the entire working range. The  
25       behaviour of this component under laser flux is shown to be excellent within the utilisation wavelength range.

      Thus, the component resisted an irradiance higher than  $80 \text{ kW/cm}^2$  by a laser emitting at a wavelength  
30       of 578 nanometres. The frequency of irradiance pulses,

each of 3 ns was 5.6 KHz and the exposure time was about five minutes.

The third example relates to the embodiment of a 3-strip antireflection treatment. The component  
5 described in this example is part of an optical parametric oscillator device (OPO). This treatment is deposited on a crystal of potassium and titanyl phosphate ( $\text{KTiPO}_4$ ) generally referred to as KTP, which is submitted to laser irradiation at 1064 nm. The  
10 properties of the crystal are such that this irradiation induces an emission of photons at 1572 and 3292 nm. The aim of the treatment is to eliminate the parasitic reflections at these wavelengths in order to improve the OPO performances. Figure 8 shows the  
15 transmission values of a silica substrate within the range 800-2600 nm treated with a stack of 10 layers of  $\text{HfO}_2$  and  $\text{SiO}_2$  of total thickness 2300 nm. The representation of this treatment on the KTP crystal would not aid the understanding of the invention, and  
20 therefore it has not been shown. Measurements of residual reflectivity on the KTP crystal are, at the working wavelengths:

- R = 0.1% at 1064 nm
- R = 0.01% at 1572 nm
- 25 -R < 7% at 3292 nm

The laser damage threshold at 1064 nm is  $23 \text{ J.cm}^{-2}$ , which is remarkable for a low reflection treatment at this wavelength; in fact the quasi-totality of the flux crosses the component and stresses the stack assembly.

Example of an embodiment of the process according to the invention

Information relating to the process for producing hafnia layers according to the invention has already  
 5 been given above.

For the three examples of embodiments described above, the production conditions were in compliance with the following table:

	HfO <sub>2</sub> layer	SiO <sub>2</sub> layer
Crucible	Without crucible or in graphite	Without crucible
Departure material	Hf metal turnings (1-3 mm)	SiO <sub>2</sub> granules
Electron gun	10 kV $\approx$ 400 mA	10 kV $\approx$ 200 mA
O <sub>2</sub> pressure	4.10 <sup>-4</sup> mbar	without O <sub>2</sub> addn.
Deposit rate	0.25 nm/sec	0.45 nm/sec
Deposit temp.	ambient	ambient

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There is a significant difference from prior art: as can be seen, the temperature of deposit substrate is equal to the ambient temperature, that is about 20°C and not 200°C as in prior art.

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